

(19) Japan Patent Agency (JP)  
(12) Disclosed Patent Gazette (A)  
(11) Patent Application Disclosure No. Hei 5-208870  
(43) Disclosure date: August 20, 1993

(51) Int. Cl. C 04 B 35/58  
Identification No. 102 D  
Agency Internal Handling No. 8821-4G  
Examination Not Requested  
No. of Claims 2 (Total of 4 pages)

(21) Application No. Hei 4-14988  
(22) Application Date: January 30, 1992  
(71) Applicant: Toshiba Corp. (000003078), 72 Banchi, Horikawa-cho, Saiwai-ku, Kawasaki City, Kanagawa Prefecture  
(72) Inventor: Tsuneji Kameda, Toshiba Corp., Keihin Office, 2-4, Suehiro-cho, Tsurumi-ku, Yokohama City, Kanagawa Prefecture  
(72) Inventor: Masahiro Asayama, Toshiba Corp., Keihin Office, 2-4, Suehiro-cho, Tsurumi-ku, Yokohama City, Kanagawa Prefecture  
(74) Representative: Saichi Suyama, patent attorney

(54) [Name of Invention] Silicon Nitride Sintered Body

(57) [Abstract]  
[Object]

To provide a silicon nitride sintered body with superior oxidation-resistance characteristics, while maintaining the strength characteristics inherent in silicon nitride.

[Constitution]

A sintered body created by forming and sintering a compound including at least 1-10% ytterbium oxide by weight and 1-10% aluminum nitride by weight as a sintering aid, with the remainder essentially being silicon nitride. The parent phase of the silicon nitride sintered body consists of  $\beta$  -  $\text{Si}_3\text{N}_4$  and/or  $\alpha'$  -  $\text{Si}_3\text{N}_4$ . A crystalline complex oxide containing Yb is present, at least at the grain boundaries of the sintered body's parent phase.

[Claims]

[Claim 1] A silicon nitride sintered body created by forming and sintering a compound including at least 1-10% ytterbium oxide by weight and 1-10% aluminum nitride by weight as a sintering aid, with the remainder essentially being silicon nitride.

[Claim 2] A silicon nitride sintered body wherein the sintered body's parent phase

consists of  $\beta$  -  $\text{Si}_3\text{N}_4$  and/or  $\alpha'$  -  $\text{Si}_3\text{N}_4$ , and a crystalline complex oxide containing Yb is present, at least at the grain boundaries of said sintered body's parent phase.

[Detailed Explanation of the Invention]

[0001]

[Field of Industrial Utilization]

The present invention relates to silicon nitride sintered bodies with superior oxidation resistance characteristics.

[0002]

[Prior Art]

Ceramic structural materials that have been conventionally used mainly include silicon nitride sintered bodies, silicon carbide sintered bodies, and SiAlON sintered bodies whose main component elements are Si-Al-O-N. Of these, the silicon nitride sintered bodies possess greater strength than the silicon carbide sintered bodies or SiAlON sintered bodies, and also possess such other characteristics as superior fracture toughness values, and attempts at their application as various kinds of high-strength, heat-resistant structural materials have been made in automobile parts materials, gas turbine fans, and other sectors.

[0003]

However, silicon nitrides themselves exhibit extremely poor sinterability, and a wide variety of sintering methods have been tried in the past, with the main methods in use currently involving liquid-phase sintering through the use of additives. Some of the additives that have worked as sintering aids for the aforesaid silicon nitrides include oxides of rare earth elements, magnesium oxide, aluminum oxide, and aluminum nitride, etc., as well as oxides, carbides, and silicides, etc., of hafnium, tantalum, and niobium, etc., and they have been used either singly or in combination. Some of the combinations of sintering aids known include, for example, yttrium oxide-aluminum oxide-aluminum nitride-oxides of Hf, Ta, Nb, etc. (see Examined Patent Application Hei 1-16791), oxides of rare earths-oxides of Hf, Ta, Nb, etc., or oxides of rare earths-oxides of Hf, Ta, Nb, etc.,-aluminum nitride (see Laid-open Patent Application Sho 60-290718), etc.

[0004]

[Problems the Invention Is to Solve]

However, since silicon nitride sintered bodies that used the kind of aforesaid sintering aids temporarily formed liquid phases during sintering, and these liquid phases were used to obtain a finely textured sintered body, liquid-phase-forming components would still remain after sintering at the grain boundaries, which would lead to the problem of formation of a grain boundary structural phase and deterioration in oxidation resistance. In other words, although yttrium oxide has been most often used as a sintering aid, silicon nitride sintered bodies that use yttrium oxide form an intergranular phase containing yttrium, leading to particular susceptibility to oxidation at high temperatures, and resulting

in a major problem with deterioration of strength in high-temperature atmospheres.

[0005]

As described above, while the yttrium oxide used as a sintering aid for silicon nitride makes possible a finely textured silicon nitride sintered body with superior mechanical strength, it also induces compounds after sintering that contain yttrium at the grain boundaries, resulting in the problem of deterioration of oxidation resistance. For this reason, it is highly desirable to obtain a silicon nitride sintered body with superior oxidation resistance characteristics, without much degradation of sintered body density and mechanical strength, etc.

[0006]

The present invention was conceived to resolve these issues, and its object is to provide a silicon nitride sintered body with superior sintered body density and mechanical strength, as well as superior oxidation resistance characteristics.

[0007]

[Methods for Resolving the Problems, and Operation]

The silicon nitride sintered body of the present invention is characterized as being created by forming and sintering a compound including at least 1-10% ytterbium oxide by weight and 1-10% aluminum nitride by weight, with the remainder essentially being silicon nitride. In addition, the silicon nitride sintered body of the present invention is characterized in that the sintered body's parent phase consists of  $\beta$  -  $\text{Si}_3\text{N}_4$  and/or  $\alpha'$  -  $\text{Si}_3\text{N}_4$ , and that a crystalline compound containing Yb is present, at least at the grain boundaries of the aforesaid sintered body's parent phase.

[0008]

The silicon nitride constituting the main material for the silicon nitride sintered body of the present invention has an average grain diameter of 1  $\mu\text{m}$  or less, and more than 80% of the structural phase should be the  $\alpha$  phase. A finer average grain diameter is desirable since it means greater sinterability. The sintered body's parent body, formed from this kind of silicon nitride material, takes its main structural phase from the  $\beta$  -  $\text{Si}_3\text{N}_4$  phase, and includes, for example, the  $\alpha'$   $\text{Si}_3\text{N}_4$  phase at a ratio of about 10% or less.

[0009]

In addition, the ytterbium oxide used as the sintering aid of the present invention functions as a sintering promoter for the silicon nitride, and remains after sintering as a high-melting-point crystalline compound at the grain boundaries. Here, the crystalline compound that includes Yb and remains at the grain boundaries is formed mainly with materials other than AlN.

[0010]

Because the aforesaid crystalline compound containing Yb exhibits little movement of atoms even when subjected to high-temperature atmospheres, there is little deterioration in the oxidation resistance characteristics of the silicon

nitride sintered body. For example, silicon nitride sintered body that uses yttrium oxide as a sintering aid has Y-Si-Al-O-N compounds existing at its grain boundaries. These Y-Si-Al-O-N compounds allow Y to move toward the surface when subjected to high-temperature atmospheres, and it appears that this causes deterioration in the sintered body's oxidation resistance characteristics. In other words, the silicon nitride sintered body of the present invention is able to maintain good oxidation resistance even in high-temperature atmospheres because it restricts oxidation related to movement of grain boundary constituents, like that described above.

[0011]

The additive volume of ytterbium oxide should be 1-10% by weight of the total composition, with the most desirable range at 3-10% by weight. When the additive volume of ytterbium oxide is less than 1% by weight, it fails to attain an adequate sintering promotion function, and if it exceeds 10% by weight, the ratio of the parent phase falls too relatively low for the original characteristics of the sintered body to be obtainable. Furthermore, the raw material for the ytterbium oxide can also be a compound such as a silicide, carbide, boride, etc., made into an oxide by heating.

[0012]

In addition, aluminum nitride supports the ytterbium oxide sintering promotion effect, promotes liquid-phase sintering of silicon nitrides, and contributes to recrystallization of the formed liquid phase. However, too much of the material will impede the sintering, so the additive volume is kept to 10% or less by weight. And since too little can make it too difficult to adequately form the liquid phase, the additive should be at least 1% or more by weight. The most desirable additive volume for aluminum nitride is in the range of 3-6% by weight.

[0013]

The desirable range for these constituents added as sintering aids comes to a total of 4-20% by weight of the total composition. This is because if the total additive volume is less than 4% by weight, it fails to attain an adequate liquid phase sintering promotion effect, and if it exceeds 20% by weight, it impedes the original characteristics of the silicon nitride.

[0014]

The silicon nitride sintered body of the present invention is obtained by first forming into the required shape a compound containing each of the above-described constituents at ratios within the prescribed ranges, and then sintering it at a temperature of about 1600°C-1900°C in an inactive atmosphere. Note that the so-called normal pressure sintering method can be used for this sintering to obtain a fine-textured silicon nitride sintered body with superior oxidation resistance characteristics. Other sintering methods such as, for example, the atmospheric pressure sintering method, the hot press method, and the hot isostatic sintering method (HIP), or some combination thereof, can also be used to obtain sintered

bodies with the requisite performance.

[0015]

[Implementation Examples]

Here follow explanations of some implementation examples for the present invention.

[0016]

Implementation Example 1

To an  $\text{Si}_3\text{N}_4$  ( $\alpha$  phase 95%) powder with an average grain diameter of 0.8  $\mu\text{m}$ , we mixed in  $\text{Yb}_2\text{O}_3$  powder 5% by weight, with average grain diameter of 1.2  $\mu\text{m}$ , and  $\text{AlN}$  powder 2% by weight, with average grain diameter of 1.0  $\mu\text{m}$ , and used a ball mill to knead it for about 24 hours and created a raw material powder. Next, for 100 parts of the raw material powder, we added and mixed in 5 parts of binder, and after further sufficient mixing, we used a press mold to manufacture a sheet body of length 50 mm  $\times$  width 50 mm  $\times$  thickness 7 mm.

[0017]

Then, we subjected the above body to a degreasing process in a nitrogen gas atmosphere, and then performed normal pressure sintering for four hours at 1750°C in the nitrogen gas atmosphere, to obtain a sintered body with silicon nitride as its main constituent.

[0018]

Applying X-ray diffraction to analyze the structural phase of the silicon nitride sintered body obtained above, we found that 86% of the parent phase was  $\beta$  -  $\text{Si}_3\text{N}_4$  phase, and the remaining 14% was  $\alpha'$  -  $\text{Si}_3\text{N}_4$  phase. A crystalline compound containing Yb was also found at the grain boundaries of the  $\text{Si}_3\text{N}_4$  crystal grains.

[0019]

Also, for comparison with the present invention, we used a raw material powder created by taking the  $\text{Si}_3\text{N}_4$  ( $\alpha$  phase 95%) used in Implementation Example 1 above, and adding  $\text{Y}_2\text{O}_3$  powder (average grain diameter of 1.0  $\mu\text{m}$ ) 5% by weight, and  $\text{AlN}$  powder 4% by weight, and manufactured a sintered body under the same conditions as Implementation Example 1.

[0020]

We performed 3-point bending strength measurement on the silicon nitride sintered bodies created in the Implementation Example and the Comparison Example at room temperature and at 1250°C. In addition, we subjected these sintered bodies to a thermal process for 100 hours at 1400°C in the air, and then looked for the amount of increased oxidation (increased weight) per sample unit area. Furthermore, we performed a 3-point bending strength measurement after the thermal process. The results are shown in Table 1.

[0021]

[Table 1]

	3-point bending strength (MPa)		After 1400°C × 100 hours of thermal process	
	Room temp.	1250°C	Oxide weight increase (mg/cm <sup>2</sup> )	3-point bending strength (MPa)
Implementation Example 1	900	750	0.29	880
Comparison Example 1	1000	800	4.76	700

As is clear from the measurement results shown in Table 1, while the silicon nitride sintered body from Implementation Example 1 had slightly inferior strength values when compared to the sintered body of the Comparison Example, which used Y<sub>2</sub>O<sub>3</sub> as the sintering aid, it exhibited superior oxidation resistance, while its strength after the heating process was greatly better than the Comparison Example's sintered body.

[0022]

#### Implementation Examples 2-5

We mixed the Yb<sub>2</sub>O<sub>3</sub> powder and AlN powder used in Implementation Example 1 into the Si<sub>3</sub>N<sub>4</sub> powder, in the respective ratios shown in Table 2, and used the raw material powders to conduct sintering under the same conditions as Implementation Example 1, to manufacture the respective silicon nitride sintered bodies.

[0023]

In the same way as Implementation Example 1, we measured the characteristics of each of the silicon nitride sintered bodies obtained above, and show those results, as well, in Table 2.

[0024]

[Table 2]

	Additive constituent (% by weight)	3-point bending strength (MPa)	After 1400°C × 100 hours of thermal process

		Yb <sub>2</sub> O <sub>3</sub>	AlN	Room temp.	1250°C	Oxide weight increase (mg/cm <sup>2</sup> )	3-point bending strength (MPa)
Imp Ex.	2	5	2	620	400	0.45	590
	3	5	6	600	490	0.25	580
	4	9	4	900	730	0.60	830
	5	9	5	880	700	0.54	790

[0025]

[Effect of the Invention]

As can be seen from the above explanation, silicon nitride sintered bodies of the present invention can obtain superior oxidation resistance characteristics while maintaining the strength characteristics inherent in the silicon nitride. Therefore, it makes it possible to supply suitable ceramics materials as structural materials used under various high-temperature atmospheres.

[0026]

[blank]